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Transition Metal Catalyzed Synthesis of Organmetallic Polymers

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by

Richard M. Laine

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Department of Materials Science and Engineering
University of Washington
Roberts Hall, FB-10
Seattle, WA 98195

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Transition Metal Catalyzed Synthesis of Organometallic Polymers

Richard M. Laine, Contribution from the Department of Materials Science and Engineering and, The Polymeric Materials Laboratory of the Washington Technology Center, University of Washington, Seattle, WA 98195

Abstract: Transition metal catalysts have recently been used to synthesize organo- metallic oligomers and polymers containing boron or silicon in the polymer backbone. Three types of transition metal catalyzed reactions have proven useful for organometallic polymer synthesis: (1) dehydrocoupling by self- reaction (2E-H ——> H_2 + E-E) or by reaction with an acidic hydrogen (E-H + X-H ——> H_2 + E-X); (2) redistribution of Si-H bonds with Si-O bonds, $-[MeHSiO]_x \longrightarrow MeSiH_3 + -[Me(O)_{1.5}]_y-$ and, (3) ring opening polymerization. In this review, we examine the potential utility of these catalytic methods for the synthesis of organometallic polymers. In each instance, an effort is made to illustrate the generality or lack thereof for reaction types. Relevant literature and proposed reaction mechanisms for each reaction are discussed.

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Introduction

The literature contains tens of thousands of publications and patents devoted to the synthesis, characterization and processing of polymers. Despite the fact that there are more than one hundred elements, the majority of these publications and patents concern polymers with carbon backbones. Furthermore, the limited (by comparison) number of publications on polymers that contain elements other than carbon in their backbones are typically devoted to polymers based on silicon, especially those with Si-O bonds.

This disparity is partially a consequence of the dearth of low cost organometallic feedstock chemicals potentially useful for polymer synthesis. It also derives from the lack of general synthetic techniques for the preparation of organometallic polymers. That is, by comparison with the numerous synthetic strategies available for the preparation of organic polymers, there are few such strategies available for synthesizing tractable, organometallic polymers.

In recent years, commerical and military performance requirements have begun to challenge the performance limits of organic polymers. As such, researchers have turned to organometallic polymers as a possible means of exceeding these limits for a wide range of applications that include: (1) microelectronics processing (e.g. photoresists) [1]; (2) light weight batteries (conductors and semi-conductors) [2]; (3) non-linear optical devices [3] and, (4) high temperature structural materials (e.g. ceramic fiber processing) [4,5].

These requirements also challenge the organometallic chemist to develop new, general synthetic techniques for the preparation of organometallic polymers. Unfortunately, preparative methods that have proved exceptionally useful for synthesizing organic polymers are frequently useless or unacceptable when applied to organometallic polymer syntheses. For example, the catalytic synthesis of polyolefins occupies a very large niche in organic polymer synthesis; however, these reactions require element-element double bonds in the feedstock chemicals. Element-element double bonds are relatively rare and difficult to synthesize in organometallic compounds. Consequently, this avenue for the catalytic synthesis of organometallic polymers is not viable.

It is well recognized that the only commercially successful polymers, polysiloxanes and polyphosphazenes, are synthesized by ring-opening polymerization, a process which has analogy in organic chemistry. However, it is our opinion that new, general synthetic routes to organometallic polymers will arise from chemistries with limited or without analogy in organic chemistry. In this review article, we explore the potential utility of catalytic methods of synthesizing organometallic polymers. In particular, we will focus on transition metal catalyzed dehydrocoupling reactions, redistribution reactions and ring-opening reactions.

In each instance, we will illustrate the generality of a particular reaction, discuss the literature and the proposed reaction mechanisms.

Dehydrocoupling Reactions

Dehydrocoupling reactions, as illustrated by reactions (1) and (2), offer great utility for the synthesis of organometallic polymers because H_2 is

$$2\text{E-H} \xrightarrow{\text{catalyst}} H_2 + \text{E-E} \qquad (1)$$

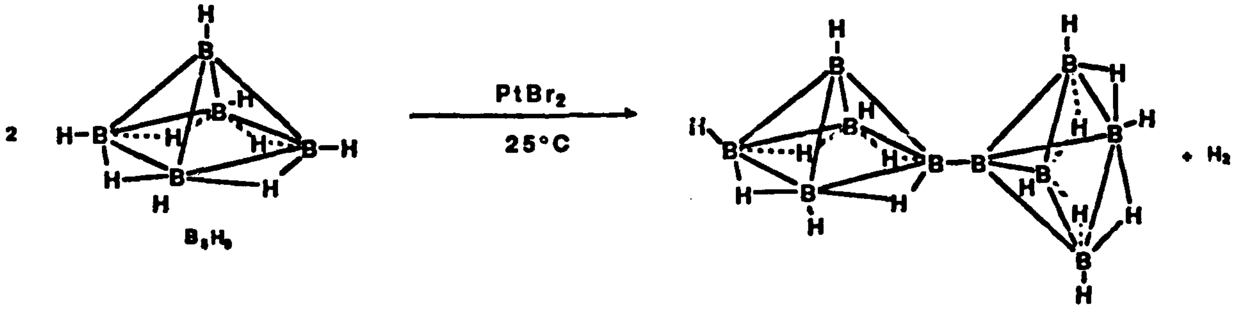
$$\text{E-H} + \text{X-H} \xrightarrow{\text{catalyst}} H_2 + \text{E-X} \qquad (2)$$

E = Element, X = O, N, S, E *etc*

generated coincident with product. H_2 is easily removed and permits one to drive a thermodynamically unfavorable reaction. Because purification procedures are minimal, the risk of contaminating a reactive and/or thermodynamically unstable polymer is minimized. If the catalyst exhibits sufficiently high activity, then its contribution to the impurity level is also minimized.

Dehydrocoupling at Boron

Transition metal catalyzed dehydrocoupling polymerization has only been observed for boron and silicon compounds. One of the earliest reports of catalytic dehydrocoupling is that Corcoran and Sneddon [6] on the catalytic dehydrocoupling of boron hydrides and carboranes, e.g. reaction (3):



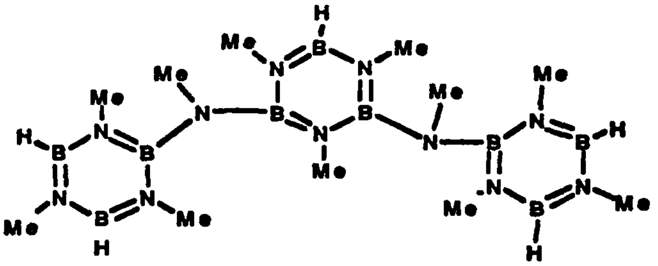
(3)

Reaction (3) is the only true instance wherein a catalyst has been used to couple B-H bonds to form H_2 and a B-B bond. Unfortunately, this reaction is extremely slow, ≤1-2 turnovers/day/mol cat even at catalyst concentrations of 10-20 mole percent of the borane reactants. Reaction rates do not improve at higher temperatures and the reaction does not lead to true polymeric species. However, recent studies with different B-H containing systems have proven more successful.

Thus, a patent by Blum and Laine [7] briefly describes ruthenium catalyzed dehydrocoupling of N-H bonds with B-H bonds to form H_2 and B-N bonds. Two of the reactions discussed in the patent are:

$$BH_3{\cdot}NMe_3 + nPrNH_2 \xrightarrow{Ru_3(CO)_{12}/60^\circ C/Benzene} \text{-}[nPrNBH]_3\text{-} + H_2 + NMe_3 \qquad (4)$$

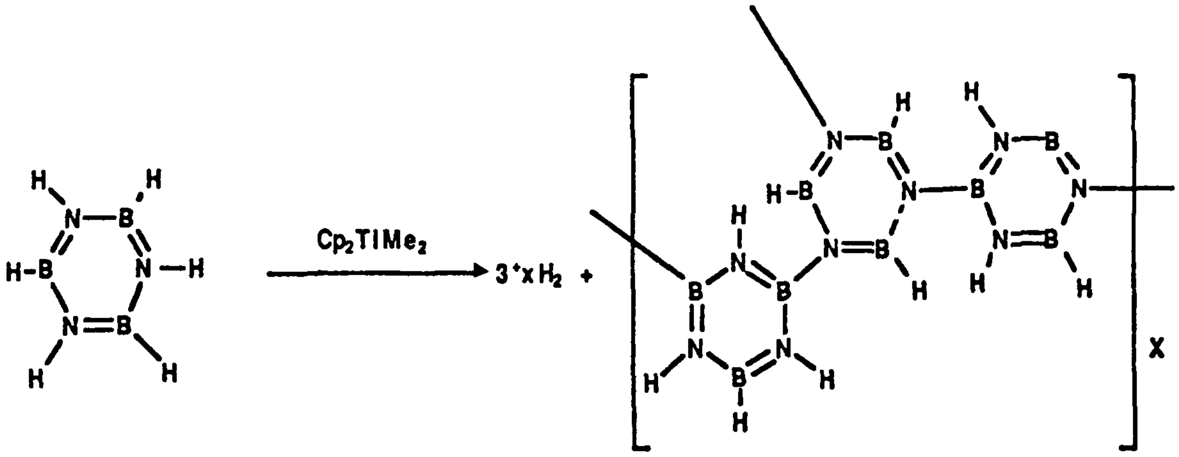
$$BH_3{\cdot}NMe_3 + MeNH_2 \xrightarrow{Ru_3(CO)_{12}/60^\circ C/Benzene} H_2 +$$



(5)

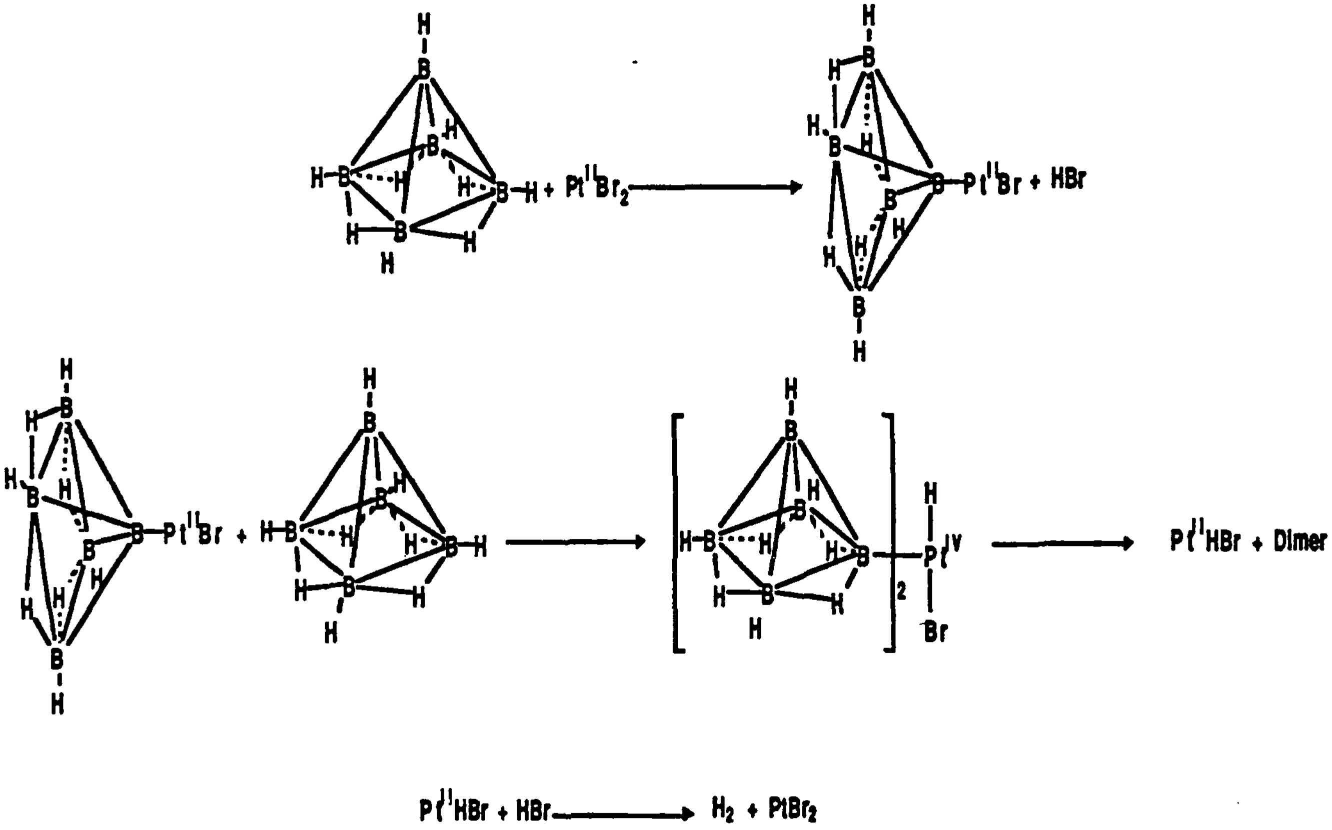
Catalyst quantities are normally 0.1mole percent of the borane complex. In the absence of catalyst, reaction (4) gives only the NMe_3 displacement product, $BH_3{\cdot}NH_2nPr$. In reaction (5), an oily oligomeric material is recovered in approximately 40% yield. Elemental and mass spectral analyses suggest that the product is the trimeric species shown; however, these results require further clarification.

More recently, Lynch and Sneddon [8,9] have begun to study reactions related to reaction (5) using borazine as substrate and $PtBr_2$, $RhCl(PPh_3)_3$ or Harrod's catalyst, dimethyl titanocene (η^5-Cp_2TiMe_2) as catalysts. These catalysts produce dimers and oligomers by B-H/N-H dehydrocoupling. In some instances fairly high molecular weights are obtained. Although complete characterization of the latter materials is not currently available, these polymers appear to be partially crosslinked [reaction (6)], as the BN:H ratio is ca. 3: 3.8 rather than 3:4 as expected for simple stepwise polymerization.


Cp₂TiMe₂
3*xH₂ +
x

(6)

Corcoran and Sneddon [6] propose a tentative mechanism for $PtBr_2$ catalyzed coupling of B-H bonds as illustrated in Scheme 1:


+ Pt^IIBr₂
Pt^IIBr + HBr
Pt^IIBr +
Pt^IV
2
Pt^IIHBr + Dimer
Pt^IIHBr + HBr
H₂ + PtBr₂

Scheme 1.

If the apical site is blocked with a methyl group, no reaction occurs. This, coupled with the exclusive formation of the 1:2'-$[B_5H_8]_2$ isomer, is consistent with a mechanism where oxidative addition occurs only at the apical site. These results are also consistent with earlier work on transition metal catalyzed hydroboration of alkynes using B_5H_9, where evidence also suggests that only the apical B-H bond is catalytically active [10].

The results illustrated by reactions (4) and (5) are preliminary and no efforts have been made to establish reaction mechanisms. The same holds true for titanocene catalysis of reaction (6). However, the following discussions on dehydrocoupling mechanisms in silicon systems, by ruthenium and titanium catalysts, most likely are relevant to dehydrocoupling as it occurs at B-H bonds.

Dehydrocouping at Silicon

The most well studied dehydrocoupling reactions are those involving Si-H bonds. Si-H dehydrocoupling can take two forms; self-reaction and reaction with acidic E-H bonds:

$$2R_3Si\text{-}H \xrightarrow{\text{catalyst}} H_2 + R_3Si\text{-}SiR_3 \qquad (7)$$

$$R_3Si\text{-}H + R'\text{-}OH \xrightarrow{\text{catalyst}} H_2 + R_3Si\text{-}OR' \qquad (8)$$

$$R_3Si\text{-}H + R'\text{-}NH_2 \xrightarrow{\text{catalyst}} H_2 + R_3Si\text{-}NHR' \qquad (9)$$

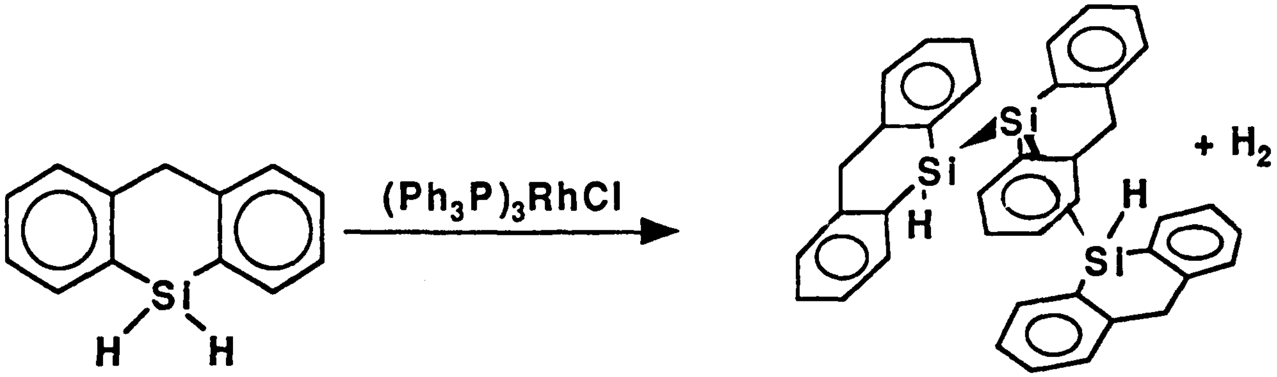
Both group 8 and early transition metals catalyzed Si-H dehydrocoupling. However, the mechanisms appear to be quite different in the two cases. The following discussions are divided along these lines.

Si-H Self-Reaction Dehydrocoupling

The earliest report of group 8 metal catalyzed self-reaction is that of Ojima et al [11], who describe the redistribution, dimerization and trimerization of simple silanes (Et_2SiH_2, $PhMeSiH_2$ and Ph_2SiH_2) in the presence of Wilkinson's catalyst, $(Ph_3P)_3RhCl$:

$$R_2SiH_2 \xrightarrow{(Ph_3P)_3RhCl/70°C} H_2 + H\text{-}[R_2Si]_n\text{-}H \quad n = 2 \text{ or } 3 \qquad (10)$$

Corey et al [12] have recently assessed reaction (10)'s synthetic utility (where $R_2SiH_2 = Ph_2SiH_2$, 9,10-dihydro-9-silaanthracene, silafluorene or dihydrodibenzosilepin) by examining the effects of variations in the reaction conditions on the rates and yields of products. Their findings indicate that low catalyst concentrations and higher temperatures favor the formation of trimer,



(11)

reaction (11). The standard reaction uses toluene as solvent, 0.25 mole percent catalyst and reaction temperatures of 20-80°C for 1-48 h. Higher reaction temperatures require less reaction time.

Under identical conditions, the order of reactivities (percent conversion to products) was found to be:

silafluorene (100)> silaanthracene (83)> Ph_2SiH_2 (59) > dibenzosilepin (10)

In a complementary study, Brown-Wensley surveyed the ablity of several group 8 metal catalyst precursors to promote dehydrocoupling of Et_2SiH_2 [13]:

$$Et_2SiH_2 \xrightarrow{\text{catalyst/RT}} H_2 + HEt_2Si\text{-}SiEt_2H \qquad (12)$$

Typical reaction conditions were 1 mole percent catalyst run in neat Et_2SiH_2 for periods of up to 75 h. The following relative activities were observed:

$(Ph_3P)_3RhCl$ (31) > $[Pd(allyl))Cl]_2$ (12) > $[Rh(CO)_2Cl]_2$ (5) > $(Ph_3P)_3Pt(C_2H_4)$ (1) $\approx$ $[Rh(COD)Cl]_2$ (1)> $Pt(COD)Cl_2$ (0.7)> $RhCl_3$ (0.3)> $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)$ (0.2) $\approx$ $[Ir(COD)Cl]_2$ (0.2) > H_2PtCl_2 (0.1) $\approx$ $(Ph_3P)_2PtCl_2$ (0.1).

Although some of the catalysts: $Pt(COD)Cl_2$, $[Pd(allyl))Cl]_2$, $[Ir(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$, were observed to dehydrocouple Et_3SiH to $Et_3Si\text{-}SiEt_3$, there was no indication that these same catalysts were able to couple $HEt_2Si\text{-}SiEt_2H$. The hydrosilylation activities of this same set of catalysts gave much the same ordering as their dehydrocoupling activities which suggests that similar initial mechanistic steps are involved in both reactions.

Despite the work of Ojima et al [11], Corey et al [12], Brown-Wensley [13], the work of Woo and Tilley [14] on catalytic dehydrocoupling with early transition metals and, the extensive work of Curtis and Epstein [15] on related chemistry, there is no concensus as to a particular mechanism for group 8 metal catalyzed self-reaction dehydrocoupling.

Ojima et al suggested a catalytic cycle, recently expanded by Woo and Tilley, that involves formation of a metal-silylene intermediate generated by α-abstraction:

$$R_2SiH_2 + M \longrightarrow R_2SiH\text{-}M\text{-}H \quad (12)$$

$$R_2SiH\text{-}M\text{-}H \longrightarrow H_2 + R_2Si{=}M \quad (13)$$

$$R_2Si{=}M + R_2SiH_2 \longrightarrow H(R_2SiH)M{=}SiR_2 \quad (14)$$

$$H(R_2SiH)M{=}SiR_2 \longrightarrow HM\text{-}SiR_2SiR_2H \quad (15)$$

or

$$R_2Si{=}M + R_2SiH_2 \longrightarrow HMSiR_2SiR_2H \quad (16)$$

$$HM\text{-}SiR_2SiR_2H \longrightarrow M + HSiR_2SiR_2H \quad (17)$$

We suggest that reactions (18) and (19) may also be operative for group 8

$$R_2Si{=}M + R_2SiH_2 \longrightarrow R_2HSi\text{-}M\text{-}SiHR_2 \quad (18)$$

$$R_2HSi\text{-}M\text{-}SiHR_2 \longrightarrow M + R_2SiH\text{-}SiHR_2 \quad (19)$$

metal catalyzed dehydrocoupling as discussed below.

The possible participation of a metal-silylene intermediate in the catalytic formation of polysilanes is supported by Zybill et al's report [16] that the HMPT stabilized iron-silylene complex, $(CO)_4Fe{=}SiMe_2$, decomposes readily to polysilanes and $Fe_3(CO)_{12}$. However, Curtis and Epstein argue that it is not necessary to invoke silylene intermediates to obtain plausible explanations for the reactions observed. In fact, silylene intermediates cannot form in the catalytic cycle leading to $Et_3Si\text{-}H$ dehydrocoupling.

If the catalytic cycle follows reactions (12)-(15) and (17), then the complete catalytic cycle would require the metal center to undergo two consecutive oxidative additions and then two consecutive reductive eliminations for a change of four electrons in each direction. Formally, the metal-silylene is formed by oxidative addition of Si-H to the metal followed by α-abstraction. Reaction (14) requires a second oxidative addition. Because it is unlikely that such a catalytic cycle would be observed for all of the metals found capable of promoting dehydrocoupling, it appears that a catalytic cycle involving reactions (16) and (17) and/or (18) and (19) is more reasonable. We believe that the disilyl intermediate shown in reactions (18) and (19) is operative in at least some catalyst systems because it permits us to explain dimerization of R_3SiH without invoking a metal-silylene complex.

Curtis and Epstein note that the nickel triad readily catalyzes H/D exchange at R_3SiH centers. If four electron redox reactions are not operative, then we must consider bimolecular reactions:

$$R_3Si\text{-}M\text{-}H + R'_3Si\text{-}M\text{-}D \longrightarrow MHD + R_3Si\text{-}M\text{-}SiR'_3 \quad (20)$$

$$MHD + R_3Si\text{-}M\text{-}SiR'_3 \longrightarrow R_3Si\text{-}M\text{-}D + R'_3Si\text{-}M\text{-}H \quad (21)$$

or

$$R_3Si\text{-}M\text{-}H + R'_3Si\text{-}M\text{-}D \longrightarrow R_3Si\text{-}D + H\text{-}M\text{-}M\text{-}SiR'_3 \quad (22)$$

$$H\text{-}M\text{-}M\text{-}SiR'_3 \longrightarrow 2M + R'_3Si\text{-}H \quad (23)$$

Other possibilities also exist. Clearly, the species $R_3Si\text{-}M\text{-}SiR'_3$ could reductively eliminate dimer coincident with MHD eliminating HD. An alternate mechanistic explanation could center on metal clusters as catalytic intermediates. Proof for these possible mechanisms, in the form of kinetic studies, is currently lacking in the literature.

Unfortunately, the group 8 metals have proved useful only for the synthesis of simple oligosilanes not for polysilanes. However, Harrod et al [17-20] have discovered that early transition metals provide quite active catalysts for the synthesis of oligo- and polysilanes. These catalysts hold much promise for the synthesis of true polysilanes via self-reaction dehydrocoupling. Harrod et al first described the catalytic dehydrocoupling of mono-substituted silanes by dimethyl titanocene, Cp_2TiMe_2 or $(\eta^5\text{-}C_5H_5)_2TiMe_2$, catalysts in 1985 [17]. Since then, the list of early transition metal catalysts that promote reaction (24) has grown to include; vanadium [18], zirconium [18], and hafnium [14].

$$xRSiH_3 \xrightarrow{\text{catalyst}} xH_2 + \text{-}[RSiH]_x\text{-} \qquad (24)$$

Harrod et al also briefly describe the successful use of thorium and uranium catalysts [18].

The oligomers produced from reaction (24), using dimethyltitanocene as catalyst, are atactic, bimodal and hydrogen terminated [19]. Vapor pressure osmometry indicates that the $PhSiH_3$ and n-hexylSiH_3 derived oligomers have molecular weights of 1000-1500 D which corresponds to DPs of about ten and narrow polydispersities. These results are corroborated by size exclusion chromatography studies (GPC) using polystyrene standards. If $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ is used, DPs of up to 20 silicon units are observed. The bimodel distribution arises because of the production of cyclic species. The all trans-hexaphenylcyclohexasilane crystallizes out of solution if the reactions are left to stand.

Titanocene catalyzed polymerization is extremely susceptible to the steric environment about silicon. Furthermore, hydrogen can compete with silane for the catalytically active site on titanium [19]. Thus, efforts to conduct valid kinetic studies and to quantitatively assess the effects of steric environment about silicon on reaction rate and product selectivity required the addition of a sacrificial alkene, reaction (25). If reaction (25) is run with the following set

$$RSiH_3 + R'CH{=}CHR' \xrightarrow{Cp_2TiMe_2/\text{toluene}/20°C} \text{-}[RSiH]_x\text{-} + R'CH_2CH_2R' \qquad (25)$$

of silanes, under identical conditions, where R'CH=CHR' = cyclohexene, the relative order of reactivities observed is:

$PhSiH_3$ (13.2) > 4-Me$PhSiH_3$ (9.8)> $MePhSiH_2$ (4.6) > $PhSiD_3$ (3.6) >
n-hexylSiH_3 (1.0) ≈ $PhCH_2SiH_3$ (1.0) > c-hexylSiH_3 (0.5)

Both c-hexylSiH_3 and $MePhSiH_2$ are unreactive except in the presence of the sacrificial alkene. Under the reaction conditions used, both silanes give only dimer products.

$MeSiH_3$ and SiH_4 were also studied under the same reaction conditions (toluene solvent, 10 mole percent catalyst). Even without the sacrificial alkene, these silanes were too reactive and difficult to work with. Both silanes tend to give intractable, highly crosslinked polymers. These results are indicative of the severe influence of steric effects at silicon and on the efficacy of the catalytic reaction.

Harrod et al have also examined the reactivity of germanes under the same conditions [20] and find that they are actually more reactive than their silicon counterparts. The only previous effort to couple germanes was that of Marchand et al [21], who find discovered reaction (26):

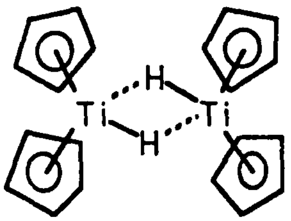
$$Et_2GeH_2 \xrightarrow{\text{steel wool/75°C}} xH_2 + H\text{-}[Et_2Ge]_x\text{-}H \quad x = 2\text{-}4 \tag{26}$$

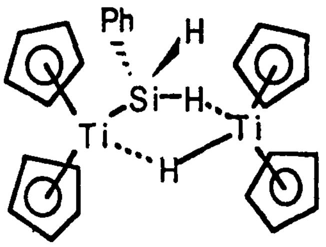
Unless care is taken, the monosubstituted germanes also react to give highly crosslinked polymers. Thus, with dimethyltitanocene, $PhGeH_3$ reacts at room temperature to give a gel. However, vanadocene (a poor catalyst for silanes) provides effective stepwise polymerization at 50°C to higher oligomers and polymers that were not further characterized.

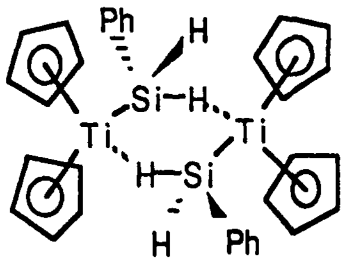
Although not useful for monosubstituted germanes, dimethyltitanocene proved to be an effective catalyst for the polymerization of Ph_2GeH_2, a reaction not possible with the analogous silane. This result is extremely important in defining a mechanism for both the silane and germane the polymerization reactions assuming the mechanisms are the same.

Harrod et al [17-20] and Tilley et al [14,22] have undertaken detailed studies to elucidate the reaction mechanisms whereby early transition metals promote self-reaction dehydrocoupling in an effort to develop better catalysts. The long term goal is to catalytically prepare high molecular weight polysilanes and polygermanes with well defined properties.

Harrod et al have isolated the following complexes from reaction solutions:







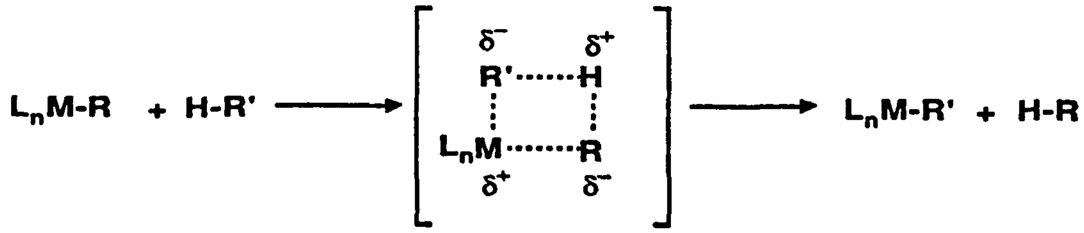
Unfortunately, these complexes do not appear to be true intermediates in the catalytic cycle. Woo and Tilley [14,22], in an effort to slow the catalytic reaction down so that intermediates can be isolated, have studied the zirconium and hafnium systems. They find that the $CpCp^*ZrClSi(SiMe_3)_3$ and $CpCp^*HfClSi(SiMe_3)_3$ (where $Cp^* = Me_5Cp$) complexes undergo stoichiometric reactions with $PhSiH_3$, reaction (27). The product of this stoichiometric reaction decomposes, reaction (28), to form $-[PhHSi]_x-$ polymers rather than oligomers:

$$CpCp^*MClSi(SiMe_3)_3 + PhSiH_3 \xrightarrow{RT(M = Zr\ or\ Hf)} HSiMe_3 + CpCp^*MClSiH_2Ph \qquad (27)$$

$$CpCp^*MClSiH_2Ph \xrightarrow{RT(M = Zr\ or\ Hf)} -[PhHSi]_x- + CpCp^*MHCl \qquad (28)$$

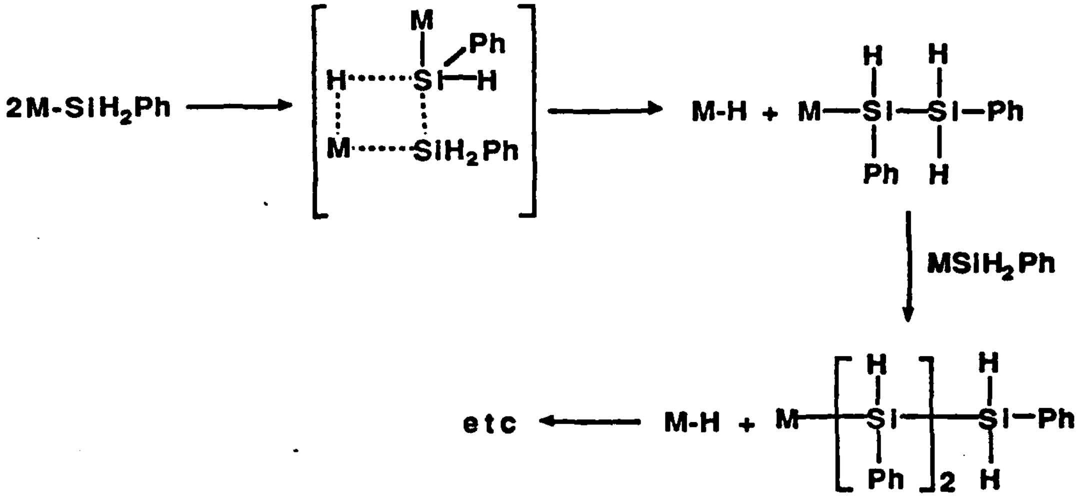
Typically, the presence of chloride substituents limits reactions to stoichiometric events or totally inhibits reaction. Thus, $Cp^*ZrSi(SiMe_3)_3Cl_2$ is inactive, while both $Cp_2Ti(SiMe_3)Cl$ and $Cp^*Ta(SiMe_3)Cl_3$ will only dimerize $PhSiH_3$. In contrast, the complex, $CpCp^*Zr(SiMe_3)Si(SiMe_3)_3$, can be used to successfully catalyze the polymerization of $PhSiH_3$ to give much higher molecular weight polymers with DPs of up to 40, coincident with the formation of cyclomers. Likewise, Chang and Corey report that in contrast to titanocene, which will dimerize $MePhSiH_2$ only in the presence of alkene, zirconocene will oligomerize $MePhSiH_2$ to give at least pentasilanes [12b].

The proposed reaction mechanism is unlike that suggested above for the group 8 metal catalysts. It probably requires σ-bond metathesis. These are reactions which have four-center transition states:



Reactions (27) and (28) are representative of a σ-bond metathesis reaction. The activation parameters for reaction (28) where M = Hf are $\Delta H^{\ddagger} = 16.4$ kcal/mol, $\Delta S^{\ddagger} \approx -27$ eu and $K_H/K_D = 2.5$. The values parallel those found for previously observed σ-bond metathesis reactions [23].

If we accept this as the likely mode of reaction, then we must still outline a reasonable catalytic cycle. Kinetic studies of the decomposition of CpCp*HfClSiH$_2$Ph to CpCp*MHCl and -[HSiPh]$_x$- reveal a second order rate dependence on [CpCp*HfClSiH$_2$Ph] with $\Delta H^{\neq} = 19.5$ kcal/mol, $\Delta S^{\neq} = -21$ eu. Woo and Tilley suggest that this indicates a four center transition state and permits them to propose a polymerization reaction such as shown in Scheme 2:



Scheme 2.

Harrod et al have argued [18] that metal-silylene-like intermediates formed by α-abstraction play a role in the early transition metal catalyzed polymerization of silanes; however, their ability to catalyze polymerization of Ph$_2$GeH$_2$ [20] provides evidence against this type of intermediate. Woo and Tilly have also explored the possibility that metal-silylene intermediates might play a role in their polymerization studies. However, when reaction (28) is carried out in the presence of silylene traps such as HSiEt$_3$, (c-hexyl)SiH$_3$, Ph$_2$SiH$_2$ or PhMeSiH$_2$, these species exhibit no influence on the course of events. Further support for the mechanism shown in Scheme 2 comes when reaction (28) (where M = Hf) is run with two equivalents of PhSiH$_3$. This reaction leads to the formation of phenylsilane dimers and trimers. With time, a new species appears that is probably the tetramer.

Further work required in the area of polysilane self-reaction dehydrocoupling is likely to focus on optimization of catalyst activity, especially with respect to the synthesis of high molecular weight polymers as there is considerable interest in polymers of this type [1]. In addition, the same driving forces for commercialization of high molecular weight polysilanes should also lead to work on the synthesis of linear polygermanes. An additional area of interest is the development of catalysts that will permit the synthesis of tractable polymethylsilane, $-[MeSiH]_x-$, and polysilane itself, $-[H_2Si]_x-$. The former is of interest as a preceramic and the latter would have many useful applications in the electronics industry.

Si-H Catalytic Reactions with E-H

The first reports describing catalytic reaction of Si-H bonds with compounds containing acidic hydrogen were those of Chalk [24] and Corriu et al [25]. These reactions involved the alcoholysis of silanes:

$$ROH + R'_3Si\text{-}H \xrightarrow{\text{catalyst}} H_2 + R'_3Si\text{-}OR \tag{29}$$

Although these reactions are not useful for the synthesis of organometallic polymers, except perhaps for polysiloxanes (where $ROH = H_2O$ and $R'_3SiH = R'_2SiH_2$), they set the stage for later work wherein the active hydrogen species is an amine [26-30]:

$$RNH_2 + R'_3Si\text{-}H \xrightarrow{\text{catalyst}} H_2 + R'_3Si\text{-}NHR \tag{29}$$

The synthesis of polysilazane oligomers via dehydrocoupling has been studied extensively by Laine et al [29, 31-35], using a variety of amine and silane reactants. For example, if Et_2SiH_2 is reacted with NH_3, reaction (30),

$$Et_2SiH_2 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60^\circ C} H_2 + \underset{y = 3\text{-}5}{-[Et_2SiNH]_y-} + \underset{x = 3\text{-}5}{H\text{-}[Et_2SiNH]_x\text{-}H} \tag{30}$$

then the major products are primarily cyclomers with the cyclotrisilazane predominating and small quantities of low molecular weight linear oligomers. Typically the catalyst concentration is 0.1 to 0.01 mole percent. Catalyst concentrations at the ppm level can be used for some reactions.

It has not been possible to prepare high molecular weight polysilazanes using reactions analogous to (30) for a variety of reasons. Modeling studies were run using reaction (31), in an effort to find the best conditions for

$$Et_3SiH + RNH_2 \xrightarrow[R = n\text{-}Pr,\ n\text{-}Bu,\ s\text{-}Bu \text{ or } t\text{-}Bu]{Ru_3(CO)_{12}/THF/70^\circ C} H_2 + Et_3SiNHR \tag{31}$$

polymer formation [31].

The kinetics and the catalytic cycle(s) for this reaction are extremely complex. In the absence of amine, the silane reacts with $Ru_3(CO)_{12}$ to produce $(Et_3Si)_2Ru_2(CO)_8$, reaction (32), which can be isolated and used in place of $Ru_3(CO)_{12}$. Catalyst concentration studies demonstrate that the rate of

$$6Et_3SiH + 2Ru_3(CO)_{12} \xrightarrow{110°C/10\ min} 3H_2 + 3(Et_3Si)_2Ru_2(CO)_8 \qquad (32)$$

reaction (31) is nonlinearly and inversely dependent on either $[Ru_3(CO)_{12}]$ or $[(Et_3Si)_2Ru_2(CO)_8]$. On a molar basis, $(Et_3Si)_2Ru_2(CO)_8$ is the more active of the two catalyst precursors. These results suggest that the true catalyst forms by cluster fragmentation. Indeed, some evidence was found for the formation of trans-$(Et_3Si)_2Ru(CO)_4$. Thus, higher catalyst concentrations do not improve reaction rates significantly.

A second problem, which also plagues self-reaction dehydrocoupling, is that the reaction rate and product selectivities are extremely susceptible to the steric environment about both silicon and nitrogen. In rate vs $[RNH_2]$ studies, the steric bulk of R controls both the reaction rate and the mechanism. The simple primary amines, n-$PrNH_2$ and n-$BuNH_2$ show an inverse, nonlinear rate dependence on $[RNH_2]$ despite the fact that they are reactants.

By comparison, the [s-$BuNH_2$] studies reveal a nonlinear positive rate dependence. On moving to the most bulky amine, t-$BuNH_2$, the rate shows almost no dependence on either [t-$BuNH_2$] or $[Et_3SiH]$. The relative global rates of reaction are $n\text{-}PrNH_2 \geq n\text{-}BuNH_2 > s\text{-}BuNH_2 \gg t\text{-}BuNH_2$. The potential product, $(Et_3Si)_2NR$, corroborated by Kinsley et al [30], is never observed with the ruthenium catalyst.

Apparently, the simple primary amines react with $Ru_3(CO)_{12}$ to form fairly stable complexes that deplete the reaction mixture of active catalyst:

$$Ru_3(CO)_{12} + EtCH_2NH_2 \longleftrightarrow (\mu^2\text{-}EtCH{=}NH)H_2Ru_3(CO)_{10} \qquad (33)$$

Hence, the inverse dependence on [n-RNH_2]. With s-$BuNH_2$, the stability of the amine ruthenium complex is sufficiently reduced such that it plays only a minor role in the catalytic cycle.

With t-$BuNH_2$, there is no α-hydrogen and the amine-ruthenium complex cannot form. However, the fact that the rate is simultaneously independent of both $[Et_3SiH]$ and [t-$BuNH_2$], is more difficult to explain and suggests that an alternate mechanism is operative. One can envision a situation in which the rate determining step is catalyst activation; however, silyl-ruthenium complexes form readily in the absence of amine. Therefore reaction of the amine at the silicon must be the rate determining step. Crabtree et al have recently studied iridium catalyzed alcoholysis of Et_3SiH and proposed that the reaction proceeds via nucleophilic attack of alcohol on a two-electron three-center Si-H···M intermediate [36]. Perhaps such an intermediate occurs in this instance. Alternately, the slow step may arise as a consequence of cluster fragmentation. The cluster fragmentation possiblity seems reasonable given that the rate vs $[Ru_3(CO)_{12}]$ studies with $t\text{-}BuNH_2$ reveal first order dependence on catalyst concentration rather than inverse dependence. These combined results suggest a catalytic cycle such as shown in Scheme 3:

$$M_3 + RCH_2NH_2 \longleftrightarrow H_2(RCH{=}NH)M_3$$

$$M_3 + 3Et_3SiH \longrightarrow 3HMSiEt_3$$

$$Et_3SiMH + Et_3SiH \longleftrightarrow H_2 + Et_3SiMSiEt_3$$

$$Et_3SiMH + RCH_2NH_2 \longrightarrow Et_3SiNHCH_2R + MH_2$$

and/or

$$Et_3SiMSiEt_3 + RCH_2NH_2 \longrightarrow Et_3SiNHCH_2R + Et_3SiMH$$

$$MH_2 \longleftrightarrow M + H_2$$

Scheme 3.

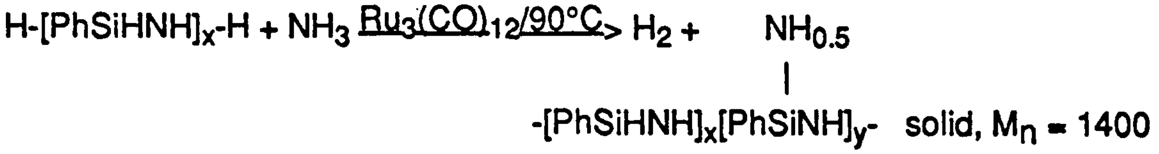
The severe steric effects observed in reaction (31) are also observed when the dehydrocoupling reaction is used to synthesize oligosilazanes. Reaction (30) exemplifies these effects. This reaction was an attempt to prepare linear, high molecular weight diethylpolysilazanes. Yet, the only products are mixtures of the cyclotrimer and cyclotetramer with low molecular weight linear species ($M_n \approx 500$ D). In contrast, the use of monosubstituted silane precursors provides access to true oligosilazanes as illustrated by reactions (34) and (35):

$$PhSiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C} H_2 + \text{-}[PhSiHNH]_x\text{-} \qquad (34)$$

$$M_n = 800\text{-}1000 \text{ D}$$

$$n\text{-}C_6H_{13}SiH_3 + NH_3 \xrightarrow{Ru_3(CO)_{12}/60°C} H_2 + \text{-}[n\text{-}C_6H_{13}SiHNH]_x\text{-} \quad M_n \approx 2700\ D \tag{35}$$

At 60°C, both oligosilazanes are essentially linear. No evidence is found for dehydrocoupling at the tertiary Si-H bonds or at the internal N-H bonds. At 90°C, the tertiary Si-H bonds react to give partially crosslinked oligosilazanes as shown for the phenylpolysilazane in reaction (36):



$$H\text{-}[PhSiHNH]_x\text{-}H + NH_3 \xrightarrow{Ru_3(CO)_{12}/90°C} H_2 + \overset{NH_{0.5}}{\overset{|}{\text{-}[PhSiHNH]_x[PhSiNH]_y\text{-}}} \quad \text{solid, } M_n \approx 1400 \tag{36}$$

Reactions (34) and (35) can be run at room temperature, if $Ru_3(CO)_{12}$ is heated (activated Ru Cat) in neat silane prior to addition of NH_3 [35].

In contrast to $PhSiH_3$ and n-hexylSiH_3, $EtSiH_3$ reacts indiscriminantly to give a crosslinked polysilazane that is sufficiently intractable to permit effective characterization. The reactivity differences found for $PhSiH_3$ and n-hexylSiH_3, when compared to $EtSiH_3$, are quite reminiscent of the reactivity differences found for $PhSiH_3$ and n-hexylSiH_3 versus $MeSiH_3$ for self-reaction dehydrocoupling as discussed by Harrod et al [19,20].

The same dehydrocoupling reaction used to synthesize simple oligosilazanes can also be used to further polymerize oligosilazanes produced via other chemical routes. Recent interest in the use of polysilazanes as silicon nitride preceramic polymers [4] originally prompted exploration of dehydrocoupling as a synthetic technique [31-35].

Oligomers of most polysilazanes ceramic precursors have been synthesized by ammonolysis of H_2SiCl_2 or $MeSiHCl_2$, as in reaction (37):

$$H_2SiCl_2 + 3MeNH_3 \xrightarrow{0°C/Et_2O} HNMe\text{-}[H_2SiNMe]_x\text{-}H + 2MeNH_3Cl \tag{37}$$

Unfortunately, these reactions lead to oligosilazanes with molecular weights too low to have useful polymeric properties. Fortunately, because they contain both Si-H bonds and N-H bonds, ruthenium catalyzed dehydrocoupling can be used to further polymerize these simple olgomers:

$$HNMe\text{-}[H_2SiNMe]_x\text{-}H \xrightarrow{Ru_3(CO)_{12}/60\text{-}90°C} \text{polymers} \tag{38}$$

When reaction (38) (where $x \approx 20$, $M_n \approx 1200$ D) is run over a 65 h period, M_n increases to only 2300 D with $M_w \approx 25,000$ D. The polysilazane viscosity changes from approximately 1-3 poise to 100 poise in the same time period. These results are typical of a gelation process. However, the GPC curve for the 65 h run [37], indicates that a significant portion of the polymer has a molecular weight well above 10K daltons.

The GPC curve is bimodal which suggests more than one mechanism for polymerization. In recent work, Youngdahl et al [35] find evidence for an additional mechanism for oligosilazane coupling. They find that the amine capped oligosilazanes produced in reaction (37), normally stable to >100°C, will condense in the presence of catalyst, reaction (39):

$$2\ \text{--SiNHMe} \xrightarrow{\text{activated Ru Cat/40°C}} \text{MeNH}_2 + \text{--Si-N(Me)-Si--} \qquad (38)$$

Two other catalytic methods of synthesizing oligo- and polysilazanes have also been discovered as discussed in the following sections.

Redistribution Reactions

Redistribution reactions, as defined here, involve the exchange of ligands or moieties between silicon centers, reaction (39):

$$\text{SiX}_n + \text{SiY}_m \overset{\text{catalyst}}{\longleftrightarrow} \text{SiX}_{n-z}\text{Y}_z + \text{SiY}_{m-z}\text{X}_z \qquad (39)$$

The use of n and m in place of 4 allows for the possibility that such catalytic exchanges may occur between penta- or hexacoordinated silicon species in addition to four coordinate silicon compounds.

Transition-metal promoted catalytic redistribution on silicon has already been well reviewed by Curtis and Epstein [15]. Some overlap between the two reviews is necessary given the different objectives; however, the majority of the work discussed below is new. In particular, the interest in this section is on the redistribution reactions of Si-H and Si-O bonds to form silisesquioxane polymers.

Curtis et al [15] have examined the utility of group 8 metal catalyzed redistribution of hydridosiloxanes, tetramethyldisiloxane in particular:

$$\text{HMe}_2\text{Si-O-SiMe}_2\text{H} \xrightarrow{(\text{Ph}_3\text{P})_2\text{Ir(CO)Cl/60°C}}$$
$$\text{Me}_2\text{SiH}_2 + \text{H(Me}_2\text{SiO)}_n\text{-SiMe}_2\text{H}\ (n = 1\text{-}6) \qquad (40)$$

In addition to Me_2SiH_2 and simple oligomers, the iridium catalyst used in reaction (40) also promotes methyl group transfer to form Me_3Si- capped oligomers. Although higher oligomers are also produced, their concentrations are small. The mechanism has already been discussed in detail and will not be covered here except to note that Curtis and Epstein state that there are discrepancies between what is suggested and the experimental evidence, especially with regard to alkyl transfers. The problem of a four electron redox process, as mentioned above, is also discussed. Further work on reaction (40) is clearly of interest in light of these discrepancies, Luo and Crabtree's results [36], and the possibility of binuclear reactions, as discussed above.

As with group 8 metal catalyzed self-reaction dehydrocoupling, group 8 metal catalyzed redistribution of hydridosiloxanes gives only oligomeric species. If the early transition metals, in particular Harrod's catalyst are used, considerable changes in product distribution are obtained.

Harrod et al [38] first described titanium catalyzed redistribution of simple hydridosiloxanes, e.g. $(EtO)_2MeSiH$ in 1986 and have recently followed up with a more detailed communication on the subject [39]:

$$(EtO)_2MeSiH \xrightarrow{Cp_2TiMe_2/RT} (EtO)_3SiMe + MeSiH_3 \qquad (41)$$

This reaction, which can be run neat or in a variety of solvents with less than 0.01 mole percent catalyst, can be used very successfully to form polydimethylsiloxane polymers from $HMe_2SiOSiMe_2H$, as in reaction (40), with Cp_2TiMe_2 catalyst. The polymers have $M_n \approx 10K$ D and a polydispersity of 1.6. The proton and silicon NMRs are indistinguishable from commercially produced polydimethylsiloxane.

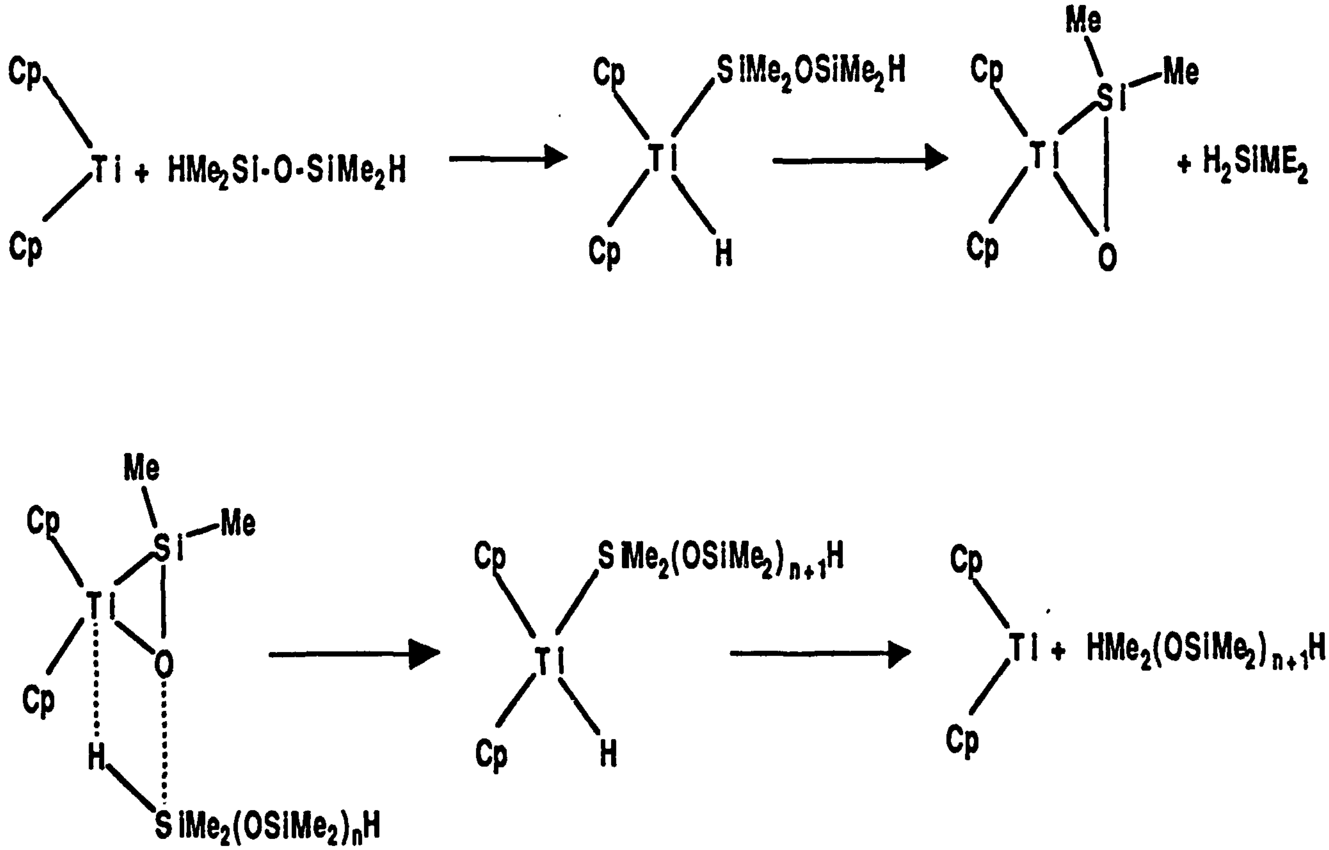
Methysilsesquioxane polymers can also be produced in a similar manner if the reactants contain -[MeHSiO]- groups, reaction (42). The source of the -[MeHSiO]- groups can either be cyclomers or linear oligomers [40]. The

$$-[MeHSiO]_x- \xrightarrow{Cp_2TiMe_2/RT/N_2} MeSiH_3 + -[MeSi(O_{1.5})]_x- \qquad (42)$$

titanocene catalyst is heat and light sensitive and, somewhat air sensitive. Reactions such as (42) typically have an induction period which can range from minutes to hours depending on the amount of oxygen present in the system. This induction period appears to be solely for catalyst activation. Once the reaction has started, the initial yellow color of the dimethyl titanocene changes rapidly to royal blue and the reaction is complete in a matter of minutes. No matter what the starting compound, if the reaction is run neat, the final product has a composition that is about $-[\mathrm{MeHSiO}]_{0.35}[\mathrm{MeSi(O_{1.5})}]_{0.65}-$. This polymer, when heated to >200°C, loses all of its -[MeHSiO]- groups to form a polymer consisting entirely of $-[\mathrm{MeSi(O_{1.5})}]_x-$, methylsilsesquioxane. The $-[\mathrm{MeSi(O_{1.5})}]_x-$ polymer is stable to greater than 500°C in nitrogen [40].

Because of the interest in new routes to polysilazanes, attempts were made to use the Harrod catalyst for redistribution of the silazane, $-[\mathrm{MeHSiNH}]_x-$ [41]. Unfortunately, the titanocene catalyst is inactive for redistribution when oxygen is replaced by nitrogen; although the solutions do turn blue. What is intriguing about this system is that if dimethyl titanocene is added to mixtures of -[MeHSiO]- and $-[\mathrm{MeHSiNH}]_x-$, then polymerization at room temperature does occur. In fact, the MeHSiO : MeHSiNH ratio can be varied from 1:1 to 1:50 without affecting the catalyst's activity. This catalyst system provides a new route to polysilazane polymers.

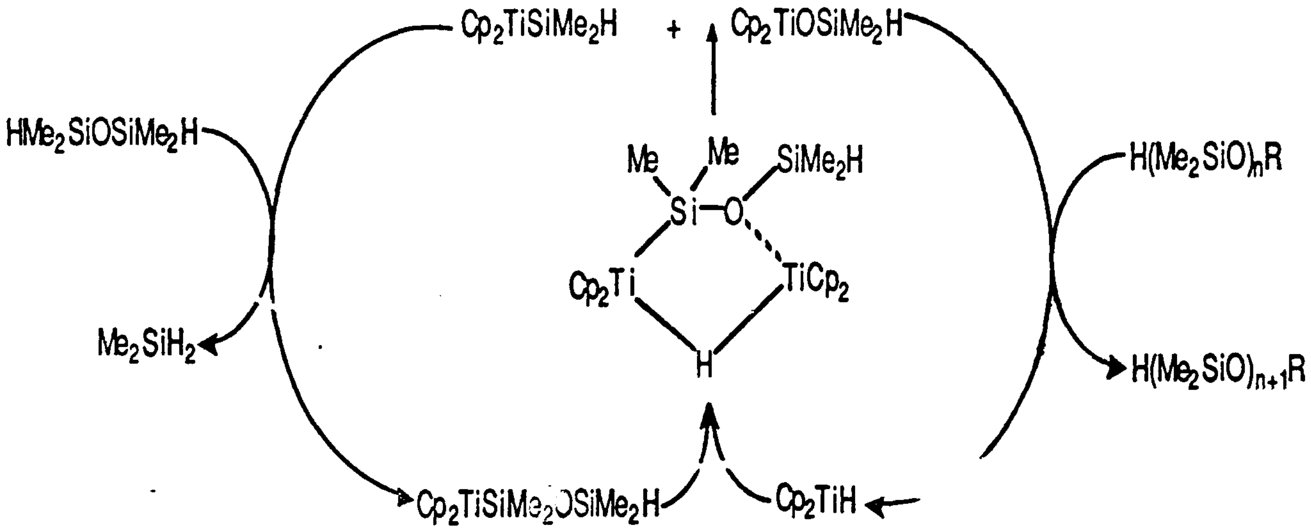
Harrod et al [39] proposed two mechanisms for reaction (40), Scheme 4


Cp
Ti + HMe₂Si-O-SiMe₂H
Cp
Cp
SiMe₂OSiMe₂H
Ti
Cp
H
Me
Cp
Si
Me
Ti
Cp
O
+ H₂SiME₂
Me
Cp
Si
Me
Ti
Cp
O
H
SiMe₂(OSiMe₂)ₙH
Cp
SMe₂(OSiMe₂)ₙ₊₁H
Ti
Cp
H
Cp
Ti + HMe₂(OSiMe₂)ₙ₊₁H
Cp

Scheme 4.

and Scheme 5, that may explain what occurs during redistribution catalysis. In

Scheme 4 the active catalyst is a mononuclear, Ti (IV) complex. In Scheme 5 catalysis requires two Ti (III) metal centers. The authors prefer the Scheme 5 mechanism because all of the species isolated from solution to date (see above) are Ti (III) species:



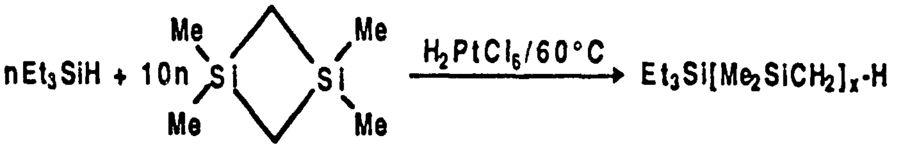
Scheme 5.

Considerably more work needs to be done on these reactions, especially in view of the silazane results, before a detailed understanding of the catalytic cycle is possible. These findings are of significant commercial interest, because the titanium catalysts offer much higher activity than possible with the group 8 metal catalysts as well as good product selectivity and, entrée to new, potentially useful silsesquioxane polymers.

Ring-Opening Catalysis

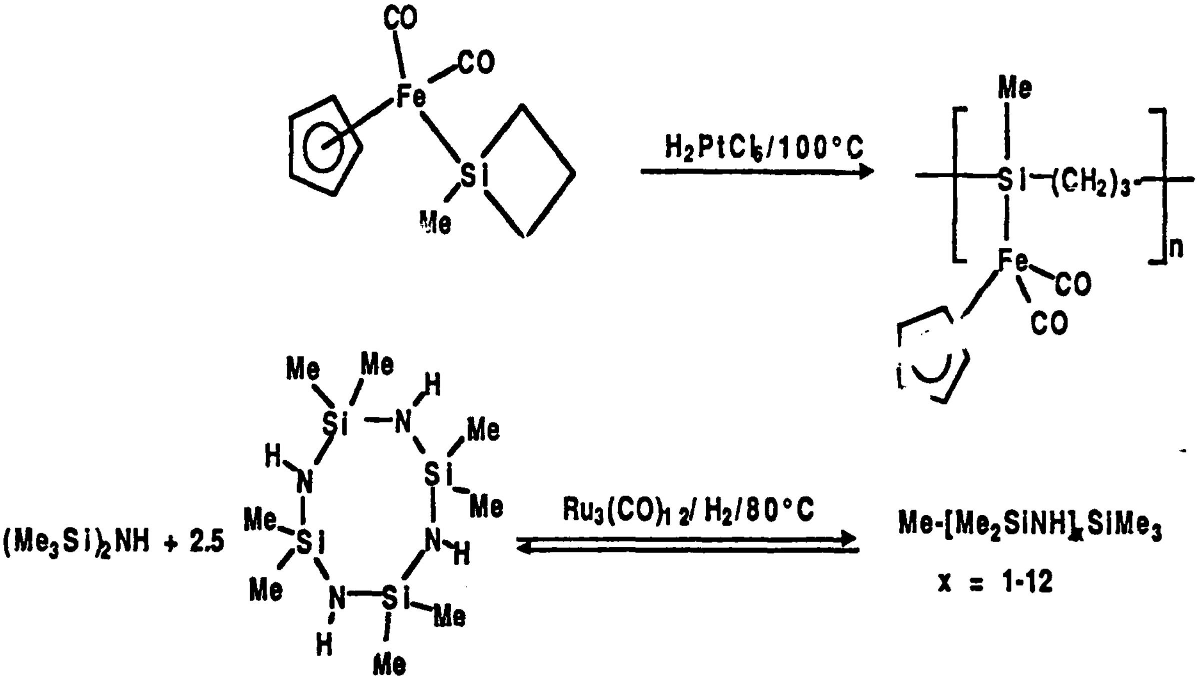
Transition metal catalyzed ring opening is the oldest reaction known for the catalytic synthesis of organometallic polymers [42,43]. Again, the only known examples involve heterocyclic monomers that contain silicon, cyclic carbosilanes or silazanes. Ring-opening polymerization of cyclic carbosilanes was discussed by Curtis and Epstein [15]. As such, discussion here is limited primarily to new developments.

Reactions (43)-(45) are examples of transition metal catalyzed ring opening polymerization [34,42-47]. Reaction (43), in the absence of a silane, provides gummy high polymers with molecular weights of 10^5 to 10^6 D. Addition of silane permits the synthesis of lower molecular weight silane capped polymers and oligomers. Reaction (44) is exceedingly interesting



nEt₃SiH + 10n
Me
Si
Me
H₂PtCl₆/60°C
Et₃Si[Me₂SiCH₂]ₓ-H

(43)



CO
Fe
Si
Me
H₂PtCl₆/100°C
Si
(CH₂)₃
n
Ru₃(CO)₁₂/H₂/80°C
(Me₃Si)₂NH + 2.5
Me
N
H
Me-[Me₂SiNH]ₓSiMe₃
x = 1-12

(44)

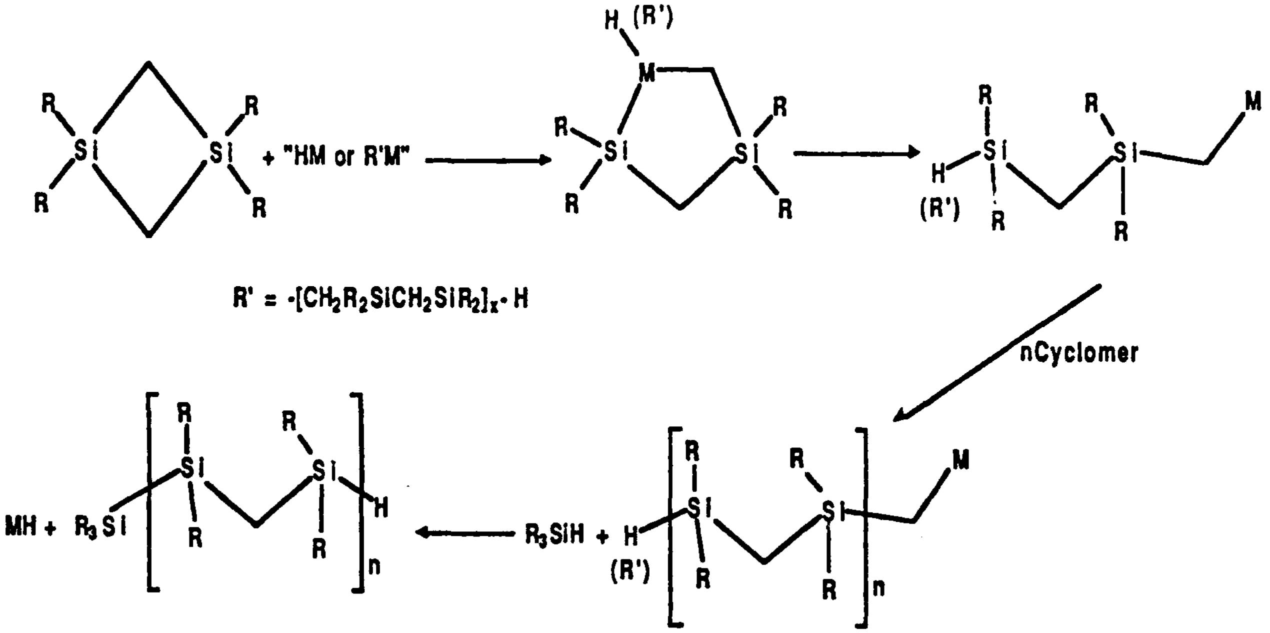
(45)

because it leads to one of the first organometallic polymers containing a pendant organometallic ligand. Reaction (44) gives similar materials although no molecular weights are reported [46]. Reaction (45) can also be run in the absence of capping agent, $(Me_3Si)_2NH$. This leads to higher molecular weight,hydrogen capped oligomers, albeit in much lower yields.

Reactions (43) and (44) are normally run at 50-150°C with less than 1 mole percent catalyst. Most of the group 8 metals will catalyze these reactions; however, platinum compounds afford the best catalyst activities.[44]

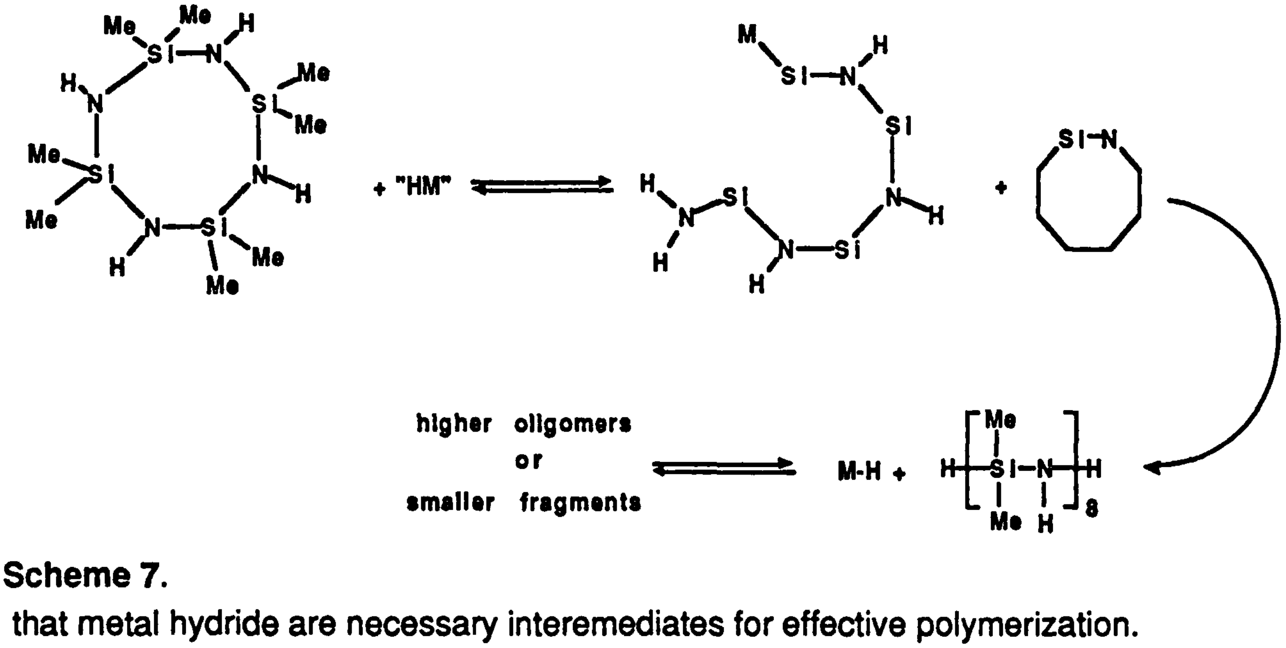
Although, several mechanisms have been proposed for reactions (43) and (44) [15,44.45]; a mechanism that fits all the facts has not been forthcoming. For example, Cundy et al [45] have suggested a catalytic sequence involving chlorine transfer polymerization; however, many catalysts and cyclic carbosilanes undergo ring opening polymerization in the absence of chlorine. Thus, such a mechanism is not likely to serve as a general model.

Scheme 6 presents a reasonable mechanistic explanation for what has been reported to date; however, it should not be considered definitive:


+ "HM or R'M"
R' = -[CH2R2SiCH2SiR2]x-H
nCyclomer
MH + R3Si
R3SiH + H
(R')

Scheme 6.

The mechanism for catalytic ring opening oligomerization of cyclosilazanes, reaction (45), as shown in Scheme 7, appears to be similar to that suggested in Scheme 6, for cyclic carbosilanes. In both cases, it is likely


+ "HM"
higher oligomers
or
smaller fragments
M-H +

Scheme 7.

that metal hydride are necessary interemediates for effective polymerization.

In fact, the introduction of 1 atm of H_2 to reaction (45), permits equilibration in 1 h at 80°C; whereas, without H_2, equilibrium is not obtained even after 24 h at 135°C. Furthermore, the $Ru_3(CO)_{12}/H_2$ (1 atm) catalyst system can be replaced with $H_4Ru_4(CO)_{12}$ without affecting the reaction rate.

At equilibrium, the 1:2.5 ratio capping agent to cyclotetrasilazane system gives a product mixture that consists of 80% polymers and 20% cyclomers with the trimer predominating. In the absence of capping agent, conversion to linear, hydrogen capped oligomers is reduced to 20% of the total products. However, the molecular weights of products recovered, following distillation of the volatiles, are oligomers with $M_n \approx 2{,}000$ D.

This approach to the preparation of high molecular weight polysilazanes is not useful because catalytic cleavage of Si-N bonds in cyclomers occurs at approximately the same rate as cleavage of Si-N bonds in the oligomers; thus, chain growth will not occur. However, the fact that equilibration is extremely rapid originally suggested the involvment of Si-H/H-N dehydrocoupling reactions during equilibration. This in turn led to the original concept of preparing polysilazane polymers via catalytic dehydrocoupling [29] as discussed above.

Future Directions

The potential utility of catalysis as a synthetic tool for the preparation of organometallic polymers is just being realized. Much of this potential remains undeveloped. Opportunities for research lie both in optimization of catalyst design and catalyst selectivity for the reactions described above. Additional opportunities most probably remain in the development of new bond forming reactions involving second and third row elements (e.g. dehydrocoupling reactions involving P-H and Ge-H bonds).

Finally, combined reactions where organometallics are copolymerized with organics may also be an extremely fruitful area of research.

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